

Phase Behavior of Poly(methyl methacrylate) and Polystyrene in Cyclohexanol: Modeling and Experiment

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Polymer solutions are very often encountered in polymer processing and knowledge of their phase behavior therefore becomes essential. Experimentally, cloud-point curves can be measured by the convenient and rapid method of thermo-optical analysis. A turbidimeter built for this purpose was used to measure, as a function of temperature and composition changes in transmitted light intensity through solutions of poly(methyl methacrylate) [PMMA] and polystyrene [PS] in a common cyclohexanol solvent. In addition, a block copolymer was also studied. The dependence of the phase boundary on polymer molecular weight was investigated. Measurements were carried out in solutions containing up to 25% polymer by weight in the temperature range 290-525 K and at the solvent vapor pressure.

Liquid-liquid separation curves for the aforementioned solutions have been modeled using two well-known equations: the Sanchez-Lacombe equation of state [SL EoS] and the UNIFAC-FV activity coefficient model (with the added free-volume contribution for application to polymer systems). Both models were implemented via a flash-algorithm. The SL EoS correctly predicts the observed upper critical solution temperature behavior in all systems and the molecular weight dependence of the cloud-point curves. Quantitative agreement of the critical temperatures was achieved by fitting the binary interaction parameter, however it was not possible to simultaneously fit the critical compositions. In contrast, UNIFAC-FV fails to predict a phase-split in the PMMA or copolymer solutions and over-predicts the UCST of the PS solution.